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(54) TREATMENT OF METAL SURFACES WITH TRIVALENT CHROMIUM SOLUTIONS

(71) We, THE LUBRIZOL CORPORATION, a corporation duly organized and existing under the laws of the State of Ohio, United States of America, c/o Box 17100 Euclid Station, Cleveland, Ohio 44117, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for treating ferrous metal and galvanized articles, and to articles thus treated.

It has been the practice for many years to form conversion coatings on metal surfaces by treatment with solutions of various chemicals which react with the surface to form a coating which protects the metal against corrosion and also serves as a paint base. Among the commonly used conversion coating compositions are aqueous phosphate and chromate solutions. Many of these are known in the art; among the simplest of the phosphate compositions are the so-called "iron phosphates" which comprise, for example, solutions of alkali metal phosphates, and which react with the iron of the ferrous metal surface to form an iron phosphate coating. Most "iron phosphate" solutions must be contacted with the metal at elevated temperatures, typically 50°C. or above. In view of the current need to conserve energy, it is of interest to develop conversion coating solutions which may be used at lower temperatures, especially room temperature.

Other conversion coating compositions in general used are the chromium-containing solutions known in the art. These generally contain hexavalent chromium in the form of chromate or dichromate, frequently in combination with trivalent chromium or in forms such that partial reduction to trivalent chromium takes place during treatment of the ferrous metal surface. Recent emphasis on water pollution problems has drawn attention to the fact that chromates are serious

pollutants. To meet water quality standards, it is frequently necessary to go through a multi-stage purification sequence in order to remove chromates from metal treatment process effluents. Typical steps in this sequence include reduction of the hexavalent chromium to trivalent chromium and precipitation with, for example, lime. The result is that the chromate content of the effluent water is decreased, frequently to zero or near zero, but the expense of the treatment process to the user is quite high.

The present invention provides a method for producing a conversion coating on a ferrous metal or galvanized article which has not previously had such a coating formed thereon which method comprises contacting said article with an aqueous solution of a trivalent chromium compound wherein the trivalent chromium ion is substantially the only ion present capable of forming a conversion coating on the article and wherein the solution contains substantially no polymeric coating material or urea nitrate or sulfamic acid. The invention is particularly suited for the treatment of steel or galvanized steel.

Solutions of chromium sulfate or chromium nitrate, for example, may be used but the preferred trivalent chromium solutions are those prepared by reduction of an aqueous hexavalent chromium-containing solution. Many suitable reducing agents, both organic and inorganic, are known. The organic ones include such materials as methanol, ethanol, ethylene glycol, formaldehyde, and hydroquinone.

The methods of reducing hexavalent chromium with organic reducing agents are generally known in the art. For example, U.S. Patents 3,063,877 and 3,404,045 describe methods for reducing chromium trioxide with formaldehyde and methanol, respectively. However, the amounts of the reducing agents used according to those patents are insufficient for complete reduction of hexavalent to trivalent chromium. Accord-

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ing to the present invention, the amount of reducing agent is increased to at least the amount required for complete reduction.

Among the suitable inorganic reducing agents are alkali metal iodides, ferrous salts, sulfur dioxide, and alkali metal sulfites or bisulfites. The alkali metal sulfites and bisulfites, notably the bisulfites and especially sodium and potassium bisulfite, are preferred. As with the organic reducing agents previously described the inorganic reducing agents are employed in amounts sufficient to completely reduce hexavalent to trivalent chromium. However, a substantial excess of sulfite or bisulfite over this amount should generally not be present since the presence of sulfite or bisulfite in the final treatment solution sometimes results in the formation of "blush rust" on the metal surface being treated. In general, the amount of sulfite or bisulfite employed should be less than a 1% excess (by weight) over the stoichiometric amount required for complete reduction of hexavalent to trivalent chromium. If, because of incomplete reaction, further reducing agent is necessary, methanol or a similar organic reducing agent, or an inorganic reducing agent other than sulfite or bisulfite, should be used to complete the reduction.

The preparation of trivalent chromium solutions which may be used (usually after dilution with water as described hereinafter) in the method of this invention is illustrated by the following Examples. All parts are by weight. Equivalents of acid are calculated on the basis of acidic hydrogens. An equivalent of a material to be oxidized or reduced is its molecular weight divided by the number of units of valence change in the oxidation-reduction reaction.

EXAMPLE 1

A solution of 51 parts (9.55 equivalents) of methanol in 144 parts of water is added dropwise, with external cooling, to a solution of 300 parts (8.96 equivalents) of 99.5% assay chromium trioxide in 204 parts of water. After methanol addition is complete, 900 parts (9.25 equivalents) of concentrated hydrochloric acid is added over several hours, with stirring, at a temperature of 44–88°C. The product is the desired trivalent chromium solution.

EXAMPLE 2

The procedure of Example 1 is repeated, except that 850 parts (9.04 equivalents) of concentrated nitric acid is used instead of HCl. A similar product is obtained.

EXAMPLE 3

The procedure of Example 1 is repeated, except that 550 parts (9.17 equivalents) of glacial acetic acid is used instead of HCl. A similar product is obtained.

EXAMPLE 4

The procedure of Example 1 is repeated,

except that 465 parts (9.12 equivalents) of concentrated sulfuric acid is used instead of HCl. A similar product is obtained.

EXAMPLE 5

Solid sodium bisulfite, 12.2 parts (0.235 equivalent), is added gradually, with stirring, to a solution of 7.8 parts (0.233 equivalent) of 99.5% assay chromium trioxide in 80 parts of water. The addition rate of the sodium bisulfite is such that the temperature does not exceed 65°C. The product is the desired trivalent chromium solution.

In the metal treatment operation in which the method of this invention is used, the metal surface is usually first cleaned by chemical and/or physical means to remove any grease, dirt and oxides. When the trivalent chromium solution contains a surfactant as described hereinafter, the initial chemical cleaning stage may be unnecessary.

The surface (or any portion thereof for which treatment is desired) is then rinsed with water and treated with the trivalent chromium solution. Treatment may be by any of the commonly used techniques such as spraying, brushing, dipping, roller-coating, reverse roller-coating, and flow-coating. The solutions of the present invention are particularly useful in a spray system. The concentration of chromium in the metal treatment solution is generally 0.01–0.2% by weight and may be somewhat lower for spray applications (e.g., 0.05–0.11%) than for immersion applications (e.g., 0.11–0.2%).

The pH of the trivalent chromium solution during application is generally 3.5–6.0, usually 4.0–5.0. Since a concentrate prepared from an already formed trivalent chromium salt (e.g., chromium chloride or nitrate), or by reduction of hexavalent chromium with certain reducing agents such as sulfur dioxide, may be too acidic to produce a metal treatment solution having a pH within this range, it may be necessary to adjust the pH of the concentrate or treatment solution by adding an alkaline reagent thereto. Such reagent (usually ammonium hydroxide, sodium hydroxide or potassium hydroxide, and preferably one of the latter two) is most preferably added to the concentrate.

On the other hand, when bisulfite is the reducing agent it may sometimes be necessary to acidify the water used for diluting the concentrate to form the treatment solution, so as to avoid the formation of a precipitate or a colloid during dilution. When this is done, the water should have a pH after adjustment below 7.0, preferably 5–5.5. The preferred acid for adjusting pH is sulfuric acid.

The temperature of application of the trivalent chromium solution to the metal surface is usually 0–50°C., although it may be

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higher (up to 75°C.) if desired, and is preferably 10—30°C. Thus, it will be appreciated that the method of this invention can use temperatures much lower than are generally required for the application of an "iron phosphate" coating, and consequently that a lower energy input is necessary. This low energy input is another advantage obtainable with the method of this invention.

Following the trivalent chromium treatment, the metal surface is usually rinsed with water, usually also at a temperature below 50°C. and advantageously at room temperature, and is then dried. Drying may be simply air-blowing at room temperature or may be at higher temperatures, usually up to 65°C.

The conversion coating produced on a ferrous metal surface by the method of this invention is usually deep blue in color. In addition to furnishing an attractive appearance to the metal, it improves corrosion resistance and paint adhesion.

After a metal article has been treated in accordance with the method of this invention, it is preferred to apply an organic coating composition which may be a siccative coating such as paint, lacquer, varnish, synthetic resin, or enamel (which are preferred), an electrostatically deposited powder coating, or any other suitable type. Examples of siccative coatings which may be used are the acrylic, alkyd, epoxy, phenolic, melamine and polyvinyl alcohol desins and paints.

Application of a siccative coating composition can be effected by any of the ordinary techniques such as brushing, spraying, dipping, roller-coating, flow-coating, electrostatic or electrophoretic attraction. The coated article is dried in the manner best suited for the siccative coating composition employed, e.g., by air-drying at ambient or elevated temperature, baking in an oven, or baking under infra-red lamps. In most instances, the thickness of the dried film of the siccative organic coating composition will be 0.1—10 mils, more often 0.3—5 mils.

From the above description, it will be apparent that the advantages obtainable using this invention include the avoidance of hexavalent chromium as a pollutant in the process effluent, lower energy requirement for formation of a conversion coating, good paint adhesion of the treated metal, and good corrosion resistance, especially of the painted metal surface.

It is within the scope of this invention to include in the trivalent chromium solution a minor amount of a surfactant, usually a non-ionic surfactant. When the surfactant is present, the chromium solution may be used as a cleaner as well as a conversion coating solution, thus eliminating the initial chemical cleaning step described hereinabove

The effectiveness of the method of this invention for forming conversion coatings on ferrous metal surfaces is demonstrated by a procedure in which panels of cold-rolled steel are cleaned by spraying with a sodium phosphate-based cleaner at 66—72°C. and rinsed with water at room temperature. They are then sprayed at 18—22°C. with a solution of Example 5. The treated panels are rinsed again with water, dried under infrared lamps and painted with a white alkyd-melamine baking enamel. Six sets of test panels are processed at the end of consecutive half-days of working of the spray line.

A set of control panels is similarly cleaned and rinsed, treated at 50—60°C. with a commercial chlorate-accelerated iron phosphate conversion coating solution having a pH of 5—6, and rinsed with water and with a commercial hexavalent-trivalent chromium post-rinse solution. These panels are also painted as described above.

The paint film on each panel is ruptured down to the bare metal by scoring a six-inch line on the surface of the panel. The scored panel is placed in a cabinet containing a 5% aqueous sodium chloride solution at 95°F. Air is bubbled through the solution to produce a corrosive salt atmosphere which acts on the surface of the test panel suspended above the level of the salt solution. The panels remain in this atmosphere for 120 hours after which they are removed, washed with water and dried with a cloth. A pressure-sensitive tape is then applied to each panel and removed suddenly. This procedure is repeated until no more paint can be removed in this manner. The loss of adhesion caused by corrosion from the scribed line is measured in thirty-seconds of an inch.

When measured in this manner, the average loss of adhesion for the panels treated by the method of this invention is 0.75 thirty-seconds of an inch. The average for the control panels is 0.44 thirty-seconds of an inch. Thus, the method of this invention gives results when the chromium solution is applied at room temperature or below, which are comparable to those provided by a commercial "iron phosphate" solution applied at elevated temperatures and followed by a commercial hexavalent chromium-containing rinse.

WHAT WE CLAIM IS:—

1. A method for producing a conversion coating on a ferrous metal article which has not previously had such a coating formed thereon which method comprises contacting said article with an aqueous solution of a trivalent chromium compound wherein the trivalent chromium ion is substantially the

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only ion present capable of forming a conversion coating on the article and wherein the solution contains substantially no polymeric coating material or urea nitrate or sulfonic acid.

2. A method according to claim 1 wherein the aqueous solution is obtained by reduction of an aqueous hexavalent chromium-containing solution.

3. A method according to claim 2 wherein the reducing agent for the hexavalent chromium is an alkali metal sulfite or bisulfite.

4. A method according to claim 3 wherein the reducing agent is sodium or potassium bisulfite.

5. A method according to claim 3 or 4 wherein the amount of sulfite or bisulfite used for reduction is less than a 1% excess, by weight, over the stoichiometric amount required for reduction of hexavalent to trivalent chromium.

6. A method according to any preceding claim wherein the metal article is rinsed with water after being contacted with said aqueous solution.

7. A method according to any preceding claim wherein the temperature of application of said aqueous solution to said article is 10–30°C.

8. A method according to any preceding claim wherein the pH of the aqueous solution is 4–6.

9. A modification of the method of any one of claims 1 to 7 wherein the article is a ferrous metal article or a galvanised article.

10. A method according to claim 9

wherein the aqueous solution contains 0.01 to 0.2% chromium by weight.

11. A method according to claim 9 or 10 wherein the pH of the aqueous solution is 3.5 to 6.

12. A method according to claim 1, wherein the solution is substantially as described in any of Examples 1 to 5.

13. A ferrous metal article having on its surface a conversion coating produced by the method of any one of claims 1 to 8.

14. A ferrous metal article according to claim 13 which has been further coated with an organic coating.

15. A ferrous metal article according to claim 13 which has been further coated with a siccative organic coating.

16. A metal article having on its surface a conversion coating produced by the method of claim 9, 10 or 11.

17. A metal article according to claim 16 which has been further coated with an organic coating.

18. A metal article according to claim 16 which has been further coated with a siccative organic coating.

19. A ferrous metal article having on its surface a conversion coating produced by the method of claim 12.

20. A ferrous metal article according to claim 19 which has been further coated with a siccative organic coating.

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